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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE. — XLV.

ON THE COMPOSITION OF PETROLEUM.

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ON THE COMPOSITION OF PETROLEUM.*

By Charles F. Mabery.

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I. THE HYDROCARBONS IN OHIO TRENTON LIMESTONE PETROLEUM WITH BOILING POINTS ABOVE 213°.

By Charles F. Mabery and O. R. Palm.

In a paper on the constituents of Pennsylvania, Ohio, and Canadian petroleum with boiling points between 150° and 220°, published several years ago,† it was shown that the distillate boiling at 212°–214° from Ohio Trenton limestone petroleum consisted of hendecane, $C_{12}H_{26}$, as a result of combustion, molecular weight determinations, and composition of its chlorine derivatives. Study of the portions with higher boiling points has since been continued for the purpose of ascertaining where the series C_nH_{2n+2} terminates and the series poorer in hydrogen appear.

The higher specific gravity of Trenton limestone petroleum and products prepared from it is well known, but the cause has not yet been explained. Since the series C_nH_{2n+2} has been found to continue in Pennsylvania petroleum in the solid forms as high as their molecular weights can be determined, and to be associated with series poorer in hydrogen above 260° (50 mm.), it was evidently interesting to ascertain the composition of the higher hydrocarbons in Ohio oil.

Results to appear later show that the series poorer in hydrogen form the chief portions of Canadian petroleum; and since the Trenton limestone oil stands in an intermediary position in its physical properties and in the properties of its distillates between Pennsylvania and Cana-

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† These Proceedings, **32**, 143 (1897).

dian crude oils, the series of hydrocarbons in Ohio oil should explain the difference in properties of commercial products obtained from it.

In resuming the study of Ohio Trenton limestone oil in 1901, a barrel of the crude oil was obtained at Welker, Ohio, which gave as its specific gravity at 20°, 0.8367. A combustion gave the following percentages of carbon, hydrogen, and sulphur: — carbon, 85.46; hydrogen, 13.91; sulphur, 0.48.

This crude oil is not so heavy as some specimens from Lima and Indiana, and the percentage of sulphur is not so high as specimens from some other fields, but it was believed to represent an average composition of Trenton limestone oil with reference to the principal series of hydrocarbons.

From 8 liters of the crude oil the portions distilling below 200°, equivalent to 1.8 liters, were removed under atmospheric pressure, and the residue was distilled *in vacuo* under a tension of 30 mm., at first within limits of 10°, which left a residue above 280° of 2000 grams. Subsequent distillation under the same tension brought the distillates together in larger quantities within certain well defined limits of temperature, indicating a greater proportion of individual hydrocarbons. After ten distillations, greater amounts collected within the following limits, and were found to represent definite hydrocarbons: 111°–113°; 129°–130°; 138°–140°; 152°–154°; 164°–168; 177°–179°; 187°–190°; 198°–202°; 213°–216°; 224°–227°; 237°–240°; 253°–255°; 263°–265°; 275°–278°. While it cannot be assumed that in a limited number of distillations the individual hydrocarbons can be separated completely, analysis and molecular weight determinations indicate that the separation is sufficiently complete to admit of identification, not only of members of the same series but of rather sudden changes from one series to the next poorer in hydrogen.

None of the fractions showed evidence of decomposition. The lower fractions were liquid, but the distillate 213°–217° was nearly solid at ordinary temperatures. The higher distillates were completely solid from paraffine, which formed a large part of these fractions. Since the solid hydrocarbons in Pennsylvania petroleum were identified as members of the series C_nH_{2n+2}, and the solid hydrocarbons in Ohio petroleum are without doubt composed of the same bodies, it was not thought worth while to examine these solids from Ohio oil. For their removal the oil was cooled to 0°, filtered, then cooled to —10°, and again filtered under pressure at the same temperature. In the higher distillates the solid hydrocarbons formed one-third or one-half of the total distillate.

The oils filtered from these fractions were very thick and viscous. Determinations of the specific gravity of the unpurified fractions at 20° gave values essentially higher than the corresponding fractions from Pennsylvania oil:

129°-130°	138°-140°	152°-154°	177°-179°	187°-190°	198°-202°
0.7998	0.8065	0.8187	0.8262	0.8351	0.8373

	224°-227°	237°-240°	253°-255°	275°-278°
(at 50°)	0.8586	0.8622	0.8849	0.8941

After removal of the solid hydrocarbon each fraction was thoroughly purified with sulphuric acid, agitating first with common concentrated acid and then with fuming acid, until the acid was nearly colorless. The heavier distillates were first dissolved in light gasoline, for they formed alone with acid an emulsion from which the oil did not readily separate. For complete removal of the acid the oil was finally washed with sodium hydrate, then dried first over calcium chloride and finally over sodium. If the oil remains unchanged after standing some time over sodium it is very well purified.

In the present state of our knowledge concerning the series of hydrocarbons poorer in hydrogen than the series C_nH_{2n+2}, definite names cannot be assigned to the members of these series. It is probable that the series C_nH_{2n} is composed of the methylene hydrocarbons, perhaps with complex side chains. The series still poorer in hydrogen may contain two or more methylene rings, but as yet there is no evidence as to what form these bodies may have.

Hydrocarbon $C_{12}H_{24}$, B. P. 211°-213°.

In a former paper * the fraction 212°-214° atmospheric pressure was shown by analysis and further identification to be dodecane, $C_{12}H_{26}$, and its specific gravity was found to be 0.7727 at 20°. This hydrocarbon was separated with others from a specimen of crude oil obtained from a well at Findlay, Ohio. Its specific gravity and composition corresponded to that of dodecane, which was separated from Pennsylvania petroleum.

The fraction 211°-213° now under examination gave as its specific gravity after thorough purification with sulphuric acid, as described above, 0.7970. A combustion gave percentages of carbon and hydrogen corresponding to the series C_nH_{2n}.

* These Proceedings, 32, 154.

I. 0.1462 gram of the oil gave 0.4590 gram CO_2 and 0.1860 gram H_2O.

II. 0.1281 gram of the oil gave 0.4020 gram CO_2 and 0.1635 gram H_2O.

III. 0.1563 gram of the oil gave 0.4906 gram CO_2 and 0.2000 gram H_2O.

	Calculated for C_nH_{2n}	Found. I.	II.	III.
C	85.70	85.62	85.53	85.61
H	14.30	14.25	14.27	14.31

The molecular weight of this hydrocarbon determined at the freezing point of benzol supported the formula $C_{12}H_{24}$.

1.1097 gram of the oil and 29.394 grams benzol gave a depression of 1°.067.

Calculated for $C_{12}H_{24}$.	Found.
168	173

The same formula was verified by the index of refraction, 1.4350, from which the molecular refraction was calculated.

Calculated for $C_{12}H_{24}$.	Found.
54.24	55.00

It is therefore evident that this hydrocarbon has the composition of the series C_nH_{2n}. The only explanation that can be offered as to the difference between it and the product with the same boiling point separated before is that the different specimens of oil coming from different sources must have differed with respect to this hydrocarbon.

Hydrocarbon $C_{13}H_{26}$, B. P. 123°–125° (30 mm.).

After ten distillations under 30 mm., 27 grams collected at 129°–130° that distilled under atmospheric pressure at 223°–225°. After careful purification the specific gravity of this distillate was found to be 0.8055 at 20°. It was shown to belong to the series C_nH_{2n} by the following combustions:

I. 0.1536 gram of the oil gave 0.4824 gram CO_2 and 0.1902 gram H_2O.

II. 0.1336 gram of the oil gave 0.4195 gram CO_2 and 0.1710 gram H_2O

	Calculated for $C_{13}H_{26}$.	Found. I.	II.
C	85.70	85.65	85.63
H	14.30	13.85	14.32

The molecular weight of this hydrocarbon determined at the freezing point of benzol corresponded to the formula $C_{13}H_{26}$.

0.9896 gram of the oil and 25.6727 grams benzol gave a depression of 1°.040.

Calculated for $C_{13}H_{26}$.	Found.
182.0	181.6

A determination of the index of refraction gave 1.4400, which corresponded to the molecular refraction:

Calculated for $C_{13}H_{26}$.	Found.
59.84	59.55

Hydrocarbon $C_{14}H_{28}$, B. P. 138°–140° (30 mm.).

After the tenth distillation 45 grams collected at 138°–140° that gave as its specific gravity at 20°, 0.8129, after thorough purification with acid. A combustion gave values for the series C_nH_{2n}.

0.1407 gram of the oil gave 0.4435 gram CO_2 and 0.1787 gram H_2O.

	Calculated for $C_{14}H_{28}$.	Found.
C	85.70	85.96
H	14.30	14.18

The formula was verified by the molecular weight found at the freezing point of benzol:

0.9552 gram of the oil and 24.5822 grams benzol gave a depression of 0°.975.

Calculated for $C_{14}H_{28}$.	Found.
196	195.2

The index of refraction was found to be 1.4437 and the molecular refraction supported the same formula:

Calculated for $C_{14}H_{28}$.	Found.
64.44	64.10

Hydrocarbon $C_{15}H_{30}$, B. P. 152°–154° (30 mm.).

A fraction of 75 grams collected at first within these limits that gradually diminished to 20 grams after the tenth distillation. After purification with acid, it gave as its specific gravity at 20°, 0.8204. A

combustion of this product gave values for carbon and hydrogen required for the series C_nH_{2n}.

0.1511 gram of the oil gave 0.4750 gram CO_2 and 0.1920 gram H_2O.

	Calculated for $C_{15}H_{30}$.	Found.
C	85.70	85.74
H	14.30	14.21

The molecular weight determined at the freezing point of benzol corresponded to the formula $C_{15}H_{30}$.

0.9370 gram of the oil and 24.2115 grams benzol gave a depression 0°.910.

Calculated for $C_{15}H_{30}$.	Found.
210	208.3

This formula was further confirmed by the index of refraction, 1.4480, which gave the following molecular refraction:

Calculated for $C_{15}H_{30}$	Found.
69.05	68.50

Hydrocarbon $C_{16}H_{32}$, B. P. 164°–168° (30 mm.).

18 grams of the oil collected within these limits after the tenth distillation that gave as its specific gravity at 20°, 0.8249. After filtration at —10°, and purification with acid, the specific gravity found was 0.8254. The proportions of carbon and hydrogen by combustion indicated the series C_nH_{2n}.

0.1536 gram of the oil gave 0.4848 gram CO_2 and 0.1945 gram H_2O.

	Calculated for $C_{16}H_{32}$.	Found.
C	85.70	86.08
H	14.30	14.16

The molecular weight at the freezing point of benzol corresponded to the formula $C_{16}H_{32}$.

1.1300 gram of the oil and 20.3767 grams benzol gave a depression of 1°.202.

Calculated for $C_{16}H_{32}$.	Found.
224	226

The index found, 1.4510, confirmed the same formula:

Calculated for $C_{16}H_{32}$.	Found.
73.65	73.08

Hydrocarbon $C_{17}H_{34}$, B. P. 177°–179° (30 mm.).

After the tenth distillation 35 grams collected within these limits with a specific gravity 0.8251 at 20°. After filtration at −10° and treatment with acid the specific gravity was raised to 0.8335. The percentages of carbon and hydrogen by combustion indicated the series C_nH_{2n}.

0.1501 gram of the oil gave 0.4720 gram CO_2 and 0.1881 gram H_2O.

	Calculated for $C_{17}H_{34}$.	Found.
C	85.70	85.76
H	14.30	14.02

The molecular weight at the freezing point of benzol determined the formula $C_{17}H_{34}$.

1.0880 gram of the oil and 24.9900 grams benzol gave a depression of 0°.896.

Calculated for $C_{17}H_{34}$.	Found.
238	238

The index of refraction, 1.4545, supported the same formula:

Calculated for $C_{17}H_{34}$.	Found.
78.25	77.50

A fraction collected at 188°–190° which should contain the next homologous hydrocarbon $C_{18}H_{36}$, but the oil was unfortunately lost by an accident during filtration from the solid.

Hydrocarbon $C_{19}H_{36}$, B. P. 198°–202° (30 mm.).

30 grams of this fraction were collected after the tenth distillation, which gave as its specific gravity at 20°, 0.8364. On cooling to −10° and filtration, 16 grams of the filtered oil was obtained with specific gravity 0.8471 at 20°. Determinations of carbon and hydrogen gave percentages which indicated a change from the series C_nH_{2n} to the series C_nH_{2n-2}.

0.1528 gram of the oil gave 0.4830 gram CO_2 and 0.1845 gram H_2O.

	Calculated for $C_{19}H_{36}$.	Found.
C	86.36	86.24
H	13.64	13.52

A determination of the molecular weight at the freezing point of benzol gave the formula $C_{19}H_{36}$.

0.9063 gram of the oil and 24.1120 grams benzol gave a depression of 0°.700.

Calculated for $C_{19}H_{36}$.	Found.
264	263

This formula was further verified by its index of refraction, which was found to be 1.4614, corresponding to the following molecular refraction:

Calculated for $C_{19}H_{36}$.	Found.
85.35	85.57

HYDROCARBON $C_{21}H_{40}$, B. P. 213°–217° (30 mm.).

The hydrocarbon $C_{20}H_{38}$ apparently did not appear, since the distillates were small, with no appearance of accumulating below 213°, at which point a larger amount was collected that proved to be the hydrocarbon $C_{21}H_{40}$. After the tenth distillation 25 grams collected that gave as its specific gravity at 20°, 0.8417. After filtration at $-10°$ the specific gravity was raised to 0.8546 at 20°. The percentages of carbon and hydrogen corresponded to the series C_nH_{2n-2}

0.1362 gram of the oil gave 0.4330 gram CO_2 and 0.1675 gram H_2O.

	Calculated for $C_{21}H_{40}$.	Found.
C	86.30	86.70
H	13.70	13.66

A determination of the molecular weight at the freezing point of benzol gave a value required for the formula $C_{21}H_{40}$.

1.1020 gram of the oil and 25.1400 grams benzol gave a depression of 0°.734.

Calculated for $C_{21}H_{40}$.	Found.
292	292.6

The index of refraction found, 1.465, also confirmed the same formula:

Calculated for $C_{21}H_{40}$.	Found.
94.56	94.45

HYDROCARBON $C_{22}H_{42}$, B. P. 224°-227° (30 mm.).

22 grams collected after the tenth distillation at 224°-227°, whose specific gravity was found to be 0.8480 at 20°. After filtration at —10° and treatment with acid in gasoline solution, the specific gravity was raised to 0.8614. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-2}.

I. 0.1403 gram of the oil gave 0.4438 gram CO_2 and 0.1670 gram H_2O.
II. 0.1571 gram of the oil gave 0.4970 gram CO_2 and 0.1901 gram H_2O.

	Calculated for $C_{22}H_{42}$.	Found. I.	Found. II.
C	86.25	86.27	86.27
H	13.75	13.31	13.53

The molecular weight determined at the freezing point of benzol corresponded to the formula $C_{22}H_{42}$.

0.8385 gram of the oil and 21.6023 grams benzol gave a depression of 0°.602.

Calculated for $C_{22}H_{42}$.	Found.
306	309

This formula was still further confirmed by the molecular weight determined at the boiling point of benzol, which gave 310.

The index of refraction, 1.4690, supported the same formula, as shown by the corresponding molecular refraction:

Calculated for $C_{22}H_{42}$.	Found.
99.16	99.60

HYDROCARBON $C_{24}H_{46}$, B. P. 237°-240° (30 mm.).

The hydrocarbon $C_{23}H_{44}$ did not appear in the small amount of distillates between 227° and 235°. Within the limits 237°-240°, 30 mm., 40 grams collected which was solid with paraffine at ordinary temperatures. After filtration at —10° the thick viscous oil gave as its specific gravity 0.8639. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-2}.

0.1515 gram of the oil gave 0.4804 gram CO_2 and 0.1855 gram H_2O.

	Calculated for $C_{24}H_{46}$.	Found.
C	86.23	86.48
H	13.77	13.70

The molecular weight determined at the freezing point gave the value required for $C_{24}H_{46}$.

1.0900 gram of the oil and 28.0340 grams benzol gave a depression of 0°.570.

Calculated for $C_{24}H_{46}$.	Found.
334	334

With hydrocarbons of such high molecular weights, the limits of accuracy in determinations by the freezing point method with the aid of solvents commonly used are reached on account of the slight depression of the freezing point.

A determination of the index of refraction gave 1.4715, which corresponds to the molecular refraction of $C_{24}H_{46}$.

Calculated for $C_{24}H_{46}$.	Found.
108.4	108

Several higher fractions were collected at points where the oil showed a tendency to accumulate, and the results of analysis indicated a series still poorer in hydrogen, C_nH_{2n-4}. 25 grams of the oil collected at 253°–255°, from which the solid was separated by filtration at −10°, and the heavy viscous oil was purified by sulphuric acid in gasoline solution. Specific gravity of the purified oil at 20° was found to be 0.8842. A combustion gave values for carbon and hydrogen required for the series C_nH_{2n-4}.

0.1424 gram of the oil gave 0.4511 gram CO_2 and 0.1718 gram H_2O.

	Calculated for $C_{23}H_{42}$.	Found.
C	86.79	86.42
H	13.21	13.49

Several attempts to determine the molecular weight of this hydrocarbon by the freezing point method failed on account of the slight depression, and the amount of oil was not sufficient for a determination by the boiling point method. The index of refraction was found to be 1.4797, which corresponds to the following molecular weight:

Calculated for $C_{22}H_{40}$.	Found.
101.7	162.1

A fraction that collected in considerable quantity at 263°–265°, 30 mm., after treatment with sulphuric acid in gasoline solution and filtration at —10°, gave as its specific gravity at 20°, 0.8864. A combustion gave the following percentages of carbon and hydrogen:

0.1470 gram of the oil gave 0.4670 gram CO_2 and 0.1752 gram H_2O.

	Calculated for $C_{24}H_{44}$.	Found.
C	86.75	86.68
H	13.25	13.32

The molecular weight of this hydrocarbon was not determined for the same reasons as the preceding. A determination of the index of refraction gave 1.4802, corresponding to the following molecular refraction:

Calculated for $C_{24}H_{44}$.	Found.
106.5	106.3

A fraction collected in quantity of 40 grams at 275°–278°, 30 mm., that was filtered at —10°, and the thick viscous oil purified with acid. It gave as its specific gravity at 20°, 0.8912. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-4}:

0.1547 gram of the oil gave 0.4914 gram CO_2 and 0.1814 gram H_2O.

	Calculated for $C_{25}H_{46}$.	Found.
C	86.71	86.66
H	13.29	13.11

The molecular weight of this hydrocarbon was not determined. The index of refraction was found to be 1.4810, and the molecular refraction as follows:

Calculated for $C_{25}H_{46}$.	Found.
110.9	110.5

While the precise formulas of the last three hydrocarbons are not determined with as complete data as those preceding, it is evident that the determinations establish the series C_nH_{2n-4}.

Ohio petroleum is therefore composed chiefly of the series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, and the series C_nH_{2n-4}. It resembles Pennsylvania petroleum in the large proportion of solid paraffine hydrocarbons. But the greater portion of the portions boiling above 216° consists of the

series C_nH_{2n}, which together with the series poorer in hydrogen explains the higher specific gravity of the crude oil and distillates prepared from it. It is probable that series still poorer in hydrogen are contained in the less volatile portions that cannot be distilled without decomposition.

The following table gives a summary of the hydrocarbons described in this paper with their boiling points and specific gravity at 20°:

HYDROCARBONS SEPARATED FROM OHIO TRENTON LIMESTONE PETROLEUM.

Series.	Symbol.	Boiling Point.		Specific Gravity at 20°.
C_nH_{2n}	$C_{12}H_{24}$	211°-213°	at. pressure	0 7970
"	$C_{13}H_{26}$	223°-225°	" "	0.8055
"	$C_{14}H_{28}$	138°-140°	30 mm.	0.8129
"	$C_{15}H_{30}$	152°-154°	" "	0.8204
"	$C_{16}H_{32}$	164°-168°	" "	0.8254
"	$C_{17}H_{34}$	177°-179°	" "	0.8335
C_nH_{2n-2}	$C_{19}H_{36}$	198°-202°	" "	0.8364
"	$C_{21}H_{40}$	213°-217°	" "	0.8417
"	$C_{22}H_{42}$	224°-227°	" "	0.8614
"	$C_{24}H_{46}$	237°-240°	" "	0.8639
C_nH_{2n-4}	$C_{23}H_{42}$	253°-255°	" "	0.8842
"	$C_{24}H_{44}$	263°-265°	" "	0.8864
"	$C_{25}H_{46}$	275°-278°	" "	0.8912

II. THE HYDROCARBONS IN CANADIAN PETROLEUM WITH HIGH BOILING POINTS.

BY CHARLES F. MABERY.

In a former paper * the constituents of Canadian Corniferous limestone petroleum distilling below 216° were described and were shown by analysis and determination of molecular weights to belong to the series C_nH_{2n+2}, to the hydrocarbon $C_{11}H_{22}$ boiling at 196°. The hydrocarbon boiling at 216° was found to be $C_{12}H_{24}$. Since several series have appeared in Pennsylvania and Ohio Trenton limestone crude oil, it seemed of interest to ascertain the series that form the main constituents of Canadian petroleum in the portions with high boiling points. The distillates separated as a part of the former work were available for the study of the higher constituents.† Examination of the fraction collected at 216° was repeated, and further results were obtained in

* These Proceedings, 32, 156 (1897).

† A part of this work was performed by Mr. E. T. Numsen, who selected it as the subject of a thesis for the degree of Bachelor of Science.

verification of the former work, which assigued the formula $C_{12}H_{24}$ to this hydrocarbon.

A determination of molecular established the formula $C_{12}H_{24}$.

0.4528 gram of the oil and 23.375 grams benzol gave a depression of 0.555.

Calculated for $C_{12}H_{24}$	Found.
168	171

The chlorine product was formed also, by the action of chlorine on the hydrocarbon standing over water. On fractioning the product it collected for the most part at 160°, 15 mm., and this distillate gave as its specific gravity at 20°, 0.9145.

The percentage of chlorine corresponded to the formula $C_{12}H_{23}Cl$.

0.1910 gram of the oil gave 0.1338 gram AgCl.

Calculated for $C_{12}H_{24}$.	Found.
17.52	17.32

The molecular weight of the chlorine product at the freezing point gave the required value for the same formula.

0.361 gram of the oil and 20.79 grams benzol gave a depression of 0°.425.

Calculated for $C_{12}H_{23}Cl$.	Found.
202.5	200

Distillation of the higher fractions was repeated several times, to collect so far as possible the hydrocarbons within narrow limits.

Hydrocarbon $C_{13}H_{26}$, B. P. 228°–230°.

The next fraction examined was the one which collected at 228°–230° after the 20th distillation. Without purification it gave as its specific gravity at 20°, 0.8087. After thorough agitation with concentrated and fuming sulphuric acid its specific gravity was reduced to 0.7979, which agrees closely with the specific gravity of the hydrocarbon $C_{13}H_{26}$ separated from Ohio petroleum.

A combustion gave values for carbon and hydrogen required for the series C_nH_{2n}.

0.1614 gram of the oil gave 0.5068 gram CO_2 and 0.2060 gram H_2O.

	Calculated for $C_{13}H_{26}$.	Found.
C	85.70	85.64
H	14.30	14.28

A determination of the molecular weight of this hydrocarbon gave values required for $C_{13}H_{26}$.

0.4631 gram of the oil and 17.79 grams benzol gave a depression of 0°.689.

Calculated for $C_{13}H_{26}$.	Found.
182	185

This formula was further verified by its index of refraction; the index found, 1.444, corresponded to the molecular refraction:

Calculated for $C_{13}H_{26}$.	Found.
59.84	60.59

The formula was still further confirmed by its chloride, which was formed by passing chlorine through the purified oil over water in diffuse sunlight until sufficient was absorbed to form the greatest yield of monochloride. After several distillations *in vacuo* a considerable portion collected at 165°, under a tension of 15 mm. A Carius determination gave the required percentage of chlorine for the monochloride.

0.1548 gram of the oil gave 0.1014 gram AgCl.

	Calculated for $C_{13}H_{25}Cl$.	Found.
Cl	16.40	16.20

The molecular weight of the chloride was determined by the freezing point method.

0.3069 gram of the oil and 19.14 grams benzol gave a depression of 0°.355.

Calculated for $C_{13}H_{25}Cl$.	Found.
216.5	220.4

The formula of the chloride was also shown by its index of refraction; the index found, 1.465, corresponded to the molecular refraction:

Calculated for $C_{13}H_{25}Cl$.	Found.
64.78	65.02

A determination of the specific gravity of the chloride gave 0.9221.

Hydrocarbon $C_{14}H_{28}$, B. P. 141°–143° (50 mm.).

After the twentieth distillation, a fraction collected in considerable quantity within the limits 141°–142°, 50 mm., that gave without purifi-

cation as its specific gravity at 20°, 0.8206. After purification with concentrated and fuming sulphuric acid, its specific gravity was reduced to 0.8099. This hydrocarbon was shown to be of the series C_nH_{2n} by determinations of carbon and hydrogen.

I. 0.1657 gram of the oil gave 0.5185 gram CO_2 and 0.2135 gram H_2O.
II. 0.1656 gram of the oil gave 0.5201 gram CO_2 and 0.2079 gram H_2O.

	Calculated for $C_{14}H_{28}$.	Found.	
C	85.70	85.34	85.65
H	14.30	14.35	14.04

The formula was shown by its molecular weight.

0.3121 gram of the oil and 18.46 grams benzol gave a depression of 0°.418.

Calculated for $C_{14}H_{28}$.	Found.
196	198

This hydrocabon gave 1.449 as its index of refraction, which corresponded to the molecular refraction of the same formula:

Calculated for $C_{14}H_{28}$.	Found.
64.44	65.02

This hydrocarbon distilled under atmospheric pressure with some decomposition at 244°–248°. Further confirmation of the formula was obtained by the composition of the chloride, which was formed in the same manner as described above. The product of chlorination was submitted to fractional distillation, which caused a considerable portion to collect at 180°, 15 mm. Specific gravity of the chloride at 20°, 0.9288. A determination of chlorine gave the percentage required for the monochloride.

0.1690 gram of the substance gave 0.1039 gram AgCl.

	Calculated for $C_{14}H_{27}Cl$.	Found.
Cl	15.40	15.21

The molecular weight of the chloride was found at the freezing point of benzol.

0.7890 gram of the substance and 23.80 grams benzol gave a depression 0°.718.

Calculated for $C_{14}H_{27}Cl$.	Found.
230.5	226.4

The index of refraction, 1.471, corresponded to the same molecular weight.

Calculated for $C_{14}H_{27}Cl$.	Found.
69.39	69.35

Another fraction of the chlorine product collected in considerable quantity at 197°–200°, 15 mm., which, after purification, distilled close at 200°, and gave as its specific gravity at 20°, 1.0066. It gave a percentage of chlorine indicating a dichloride.

0.1669 gram of the substance gave 0.1680 gram AgCl.

	Calculated for $C_{14}H_{26}Cl_2$.	Found.
Cl	26.80	24.90

The low percentage of chlorine is doubtless due to incomplete chlorination. The index of refraction found, 1.489, corresponds to the molecular refraction of the dichloride.

Calculated for $C_{14}H_{26}Cl_2$.	Found.
74.33	76.12

Hydrocarbon $C_{15}H_{30}$, B. P. 159°–160° (60 mm.).

Since a considerable portion of the distillates collected constant at 159°–160°, 50 mm., after the twentieth distillation, this fraction was selected for the identification of the next hydrocarbon, which proved to be $C_{15}H_{30}$. It gave as its specific gravity at 20°, before purification, 0.8311, and after thorough agitation with concentrated and fuming sulphuric acid, 0.8192. Determinations of carbon and hydrogen indicate the series C_nH_{2n}.

0.1586 gram of the oil gave 0.4961 gram CO_2 and 0.2007 gram H_2O.

	Calculated for $C_{15}H_{30}$.	Found.
C	85.70	85.30
H	14.30	14.16

This formula was indicated by the molecular weight determined at the freezing point of benzol.

0.3624 gram of the oil and 19.276 grams benzol gave a depression of 0°.443.

Calculated for $C_{15}H_{30}$.	Found.
210	208

The same formula was confirmed by the molecular refraction, calculated from the index found, 1.452.

Calculated for $C_{15}H_{30}$.	Found.
69.04	69.15

A portion of this hydrocarbon was chlorinated, and the product distilled until it came together in large amount at 190°, 15 mm. Its specific gravity at 20° was found to be 0.9358. Determinations of chlorine established its composition.

I. 0.1579 gram of the substance gave 0.0951 gram AgCl.
II. 0.2032 gram of the substance gave 0.1158 gram AgCl.

	Calculated for $C_{15}H_{29}Cl$.	Found. I.	Found. II.
Cl	14.45	14.55	14.09

For further identification the molecular weight of the chloride was ascertained.

0.4520 gram of the substance and 17.44 grams benzol gave a depression of 0°.529.

Calculated for $C_{15}H_{29}Cl$.	Found.
244.5	240

The index of refraction found, 1.455, corresponded to a molecular refraction of the same formula:

Calculated for $C_{15}H_{29}Cl$.	Found.
73.99	74.83

It would have been interesting to include in this examination the hydrocarbons with still higher boiling points to ascertain where the series C_nH_{2n-2} and C_nH_{2n-4} begin, for comparison with the corresponding distillates trom other petroleum. But the work described above exhausted the supply of distillates prepared from the large distillation of crude oil, and the great amount of labor involved in working up to the well distilled fractions from the crude oil prevented a repetition on account of the attention demanded by more important lines of work.

The hydrocarbons described above, representing considerable proportion of Canadian petroleum, correspond in boiling points and in composition to those separated from Ohio Trenton limestone petroleum. An explanation of the higher specific gravity of Canadian crude oil and commercial products obtained from it over Ohio, Pennsylvania, West

Virginia, Kentucky, and similar crude oils, is given by the larger proportions of the series of hydrocarbons C_nH_{2n} and series poorer in hydrogen in the Canadian oil. This series begins in the fraction 196° in the latter crude oil, much lower than in any of the other petroleums mentioned, and no doubt forms a much larger proportion of the crude oil. Doubtless the same holds true of the series still poorer in hydrogen. As shown in a former paper, the series C_nH_{2n} does not appear in Pennsylvania petroleum until the hydrocarbon $C_{17}H_{34}$ is reached; but in Canadian petroleum the first hydrocarbon of this series is $C_{11}H_{22}$. In Ohio petroleum the series begins with the hydrocarbon $C_{12}H_{24}$.

Doubtless the changes in series in the crude oil are more gradual than appears from our results. One distillation as conducted in a refinery affords only a partial separation. But in long continued fractional separations the tendency toward collection in heaps indicates an accumulation of the hydrocarbons in the vicinity of their boiling points. The smaller quantities which collect between are composed of mixtures of higher and lower boiling hydrocarbons, and doubtless the larger heap is not entirely free from higher and lower boiling constituents. Perhaps this causes a balancing of molecular weights, but it is evident that the contaminating higher and lower bodies are not sufficient in amounts to interfere with determinations that establish the formula of the principal hydrocarbon.

The following table gives the hydrocarbons separated from Canadian petroleum, and the chlorides prepared from them, with their boiling points and specific gravity:

	Symbol.	Boiling Point.		Specific Gravity at 20°.
Hydrocarbon	$C_{12}H_{24}$	216°		
Chloride	$C_{12}H_{23}Cl$	160°	15 mm.	0.9145
Hydrocarbon	$C_{13}H_{26}$	228°-230°		0.8087
Chloride	$C_{13}H_{25}Cl$	165°	" "	0.9221
Hydrocarbon	$C_{14}H_{28}$	141°-148°	50 "	0.8096
Chloride	$C_{14}H_{27}Cl$	180°	15 "	0.9288
Hydrocarbon	$C_{15}H_{30}$	159°-169°	50 "	0.8192
Chloride	$C_{15}H_{29}Cl$	190°	15 "	0.9358

III. HYDROCARBONS IN SANTA BARBARA CRUDE OIL.

Composition of California Petroleum (continued).

In a paper published two years ago,* allusion was made to a specimen of peculiar heavy petroleum that we had received from Mr. J. B. Bard-

* These Proceedings, 36, 255.

well, Summerland, Santa Barbara County, Cal., representing the heavy oil that is taken from wells sunk below the Pacific Ocean. An examination of this petroleum seemed desirable, especially since it is the heaviest specimen, with one exception, that has been examined in this laboratory. It represents the last member of a series beginning with the light yellow Berea Grit oil from Southern Ohio, which was found by O. C. Dunn and me * to be the lightest petroleum that had come to our knowledge.

This work was undertaken by Mr. C. V. Zoul.† The oil as it was received had the consistency of heavy tar; it would scarcely flow at ordinary temperatures.

Its specific gravity at 20° was found to be 0.9845. It contained 0.84 per cent sulphur and 1.25 per cent nitrogen. A combustion gave 86.32 per cent carbon, and 11.70 per cent hydrogen, showing that the crude oil is composed, at least to a large extent, of hydrocarbons poorer in hydrogen than petroleum from most other sources. In attempting to ascertain the composition of this petroleum, 2000 grams were fractioned under a tension of 60 mm., collecting within 5°. The first distillate came over at 200° atmospheric pressure, and only small amounts were collected below 175°, 60 mm. The distillation was carried to 365°, without attempting to collect closer than in 5° fractions, since the principal object was to ascertain the form of the hydrocarbons, although, as will appear, the fractions gave fairly close values for their molecular weights.

The heavy character of the constituents of this petroleum is shown by the specific gravity of several distillates after the fifth distillation.

150°-155°	305°-310°	325°-330°	240°-245°
0.8649	0.9641	0.9739	0.9778

The residue at 365° from 2000 grams was 200 grams, which showed that the greater portion of the oil distilled between 150° and 360°, or within a range of about 200°. Only 85 grams came over below 150°, 60 mm.; at higher temperatures the fractions collected in larger amounts at certain points, and these distillates were selected to ascertain the series of hydrocarbons:

	155°-160°	175°-180°	195°-200°	210°-215°
Weights,	25	70	50	75
	223°-230°	250°-255°	310°-315°	340°-345°
Weights,	75	50	80	45

* Am. Chem. Journ., **18**, 1 (1896).

† Mr. Zoul selected this work as the subject of a thesis for the degree of Bachelor of Science.

Hydrocarbon $C_{13}H_{24}$, B. P. 150°–155° (60 mm.).

Before treatment with acids, the distillate 150°–155° gave as its specific gravity at 20°, 0.8649 and 0.8621 after purification with concentrated and fuming sulphuric acid and washing with caustic soda.

A combustion gave percentages of carbon and hydrogen corresponding to the formula $C_{13}H_{24}$.

0.1357 gram of the oil gave 0.4312 gram CO_2 and 0.1653 gram H_2O.

	Calculated for $C_{13}H_{24}$.	Found.
C	86.67	86.68
H	13.33	13.62

The molecular weight of this hydrocarbon at the freezing point of benzol indicated the same formula.

0.3641 gram of the oil and 18.17 gram benzol gave a depression of 0°.541.

Calculated for $C_{13}H_{24}$.	Found.
180	181.5

A determination of the index of refraction gave 1.4681, from which the molecular refraction was calculated:

Calculated for $C_{13}H_{24}$.	Found.
57.74	58.05

Hydrocarbon $C_{16}H_{30}$, B. P. 175°–180° (60 mm.).

The refraction 175°–180° was rather thick and viscous, with a specific gravity, unpurified, at 20°, 0.8832. After purification its specific gravity was reduced to 0.8808 with comparatively little change. Percentages of carbon and hydrogen by combustion corresponded to the formula $C_{16}H_{30}$.

0.1533 gram of the oil gave 0.4879 gram CO_2 and 0 1797 gram H_2O.

	Calculated for $C_{16}H_{30}$.	Found.
C	86.48	86.82
H	13.52	13.11

A determination of molecular weight at the freezing point of benzol gave the same formula.

0.7134 gram oil and 16.56 gram benzol gave a depression of 0°.974.

Calculated for $C_{16}H_{30}$.	Found.
222	216.7

The index of refraction was found to be 1.470, which gave the molecular refraction for the formula $C_{16}H_{30}$.

Calculated for $C_{16}H_{30}$.	Found.
71.6	70.3

Hydrocarbon $C_{17}H_{30}$, B. P. 190°–195° (60 mm.).

Very little difference in specific gravity of this distillate was found before and after purification. The unpurified distillate gave 0.8969, the purified, 08919. The proportions of carbon and hydrogen by combustion indicated a change in series from C_nH_{2n-2} in the preceding hydrocarbons to C_nH_{2n-4}.

0.1444 gram of the oil gave 0.4628 gram CO_2 and 0.1664 H_2O.

	Calculated for $C_{17}H_{30}$.	Found.
C	87.18	87.40
H	12.82	12.90

Determination of the molecular weight at the freezing point of benzol gave a value for the formula $C_{17}H_{30}$.

0.8220 gram of the oil and 18.20 grams benzol gave a depression of 0°.921.

Calculated for $C_{17}H_{30}$.	Found.
234	240

The index of refraction was found to be 1.4778, corresponding to the following molecular refraction:

Calculated for $C_{17}H_{30}$.	Found.
74.03	74.27

Hydrocarbon $C_{18}H_{32}$, B. P. 210°–215° (60 mm.)

The viscous distillate 210°–215° had the specific gravity without purification 0.9085, and was not materially changed after thorough treatment with concentrated and fuming sulphuric acid in gasoline solution 0.8996. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-4}.

0.1494 gram of the oil gave 0.4787 gram CO_2 and 0.1713 gram H_2O.

	Calculated for $C_{18}H_{32}$.	Found.
C	87.10	87.38
H	12.90	12.83

An 18-carbon compound was shown by a determination of its molecular weight at the freezing point of benzol.

0.8281 gram of the oil and 18.94 grams benzol gave a depression of $0^\circ.864$.

Calculated for $C_{18}H_{32}$.	Found.
248	248

This formula was also shown by the index of refraction, which was found to be 1.484 at 20° and the molecular refraction :

Calculated for $C_{18}H_{32}$.	Found.
78.64	78.86

Hydrocarbon $C_{24}H_{44}$, P. B. 250°–255°, 60 mm.

The viscous distillate 250°–255° gave as its specific gravity at 20° 0.9299. A combustion gave values for carbon and hydrogen for the series C_nH_{2n-4}.

0.1481 gram of the oil gave 0.4745 gram CO_2 and 0.1628 gram H_2O.

	Calculated for $C_{24}H_{44}$.	Found.
C	87.42	87.40
H	12.58	12.29

Determinations of the molecular weight of this hydrocarbon at the freezing point of naphthaline gave results corresponding to the formula $C_{24}H_{44}$.

I. 0.5682 gram of the oil and 11.66 grams naphthaline gave a depression of $1^\circ.022$.

II. 0.4777 gram of the oil and 12.21 grams naphthaline gave a depression of $0^\circ.819$.

Calculated for $C_{24}H_{44}$.	Found. I.	Found. II.
332	329	330

HYDROCARBON $C_{27}H_{46}$, B. P. 310°–315° (60 mm).

This distillate was very thick and viscous. For purification it was dissolved in light gasoline, and after treatment the gasoline was distilled off with the aid of a current of CO_2. The original distillate gave the specific gravity 0.9548, which was not changed by the treatment with acid; it then gave 0.9451.

Determinations of carbon and hydrogen gave values required for the series C_nH_{2n-8}.

I. 0.1479 gram of the oil gave 0.4757 gram CO_2 and 0.1588 gram H_2O.
II. 0.1486 gram of the oil gave 0.4769 gram CO_2 and 0.1613 gram H_2O.

	Calculated for $C_{27}H_{46}$.	Found. I.	II.
C	87.59	87.72	87.52
H	12.11	12.00	12.13

A determination of its molecular weight at the freezing point of benzol gave a value required for a 27-carbon compound.

0.3985 gram of the oil and 17.488 grams benzol gave a depression of 0°.300.

Calculated for $C_{27}H_{46}$.	Found.
370	372

The same formula was supported by the index of refraction, 1.5146, from which the molecular refraction was calculated.

Calculated for $C_{27}H_{46}$.	Found.
116	118

HYDROCARBON $C_{29}H_{50}$, B. P. 340°–345° (60 mm.).

This distillate was purified as before in light gasoline. After the gasoline was removed there remained an extremely viscous oil, light yellow in color, that would scarcely flow at ordinary temperatures. Specific gravity at 20°, 0.9778. The original fraction had scarcely any odor, consequently contained no phenol derivative.

A combustion of the purified oil gave the following values for carbon and hydrogen:

0.1489 gram of the oil gave 0.4781 gram CO_2 and 0.1634 gram H_2O.

	Calculated for $C_{29}H_{50}$	Found.
C	87.44	87.76
H	12.56	12.28

The higher distillates were not examined, since the results described above are sufficient to establish the composition of the main body of the crude oil. The difficulties in obtaining hydrocarbons at these high temperatures at all well fractioned, and analytical values to decide their composition, are very great. It is evident that the series of hydrocarbons which compose Santa Barbara petroleum explain the peculiar nature of this oil, which is unlike any other petroleum that has been examined in this laboratory. The most volatile distillates are composed of the series C_nH_{2n-2}, and the proportions of hydrogen gradually fall off through the series C_nH_{2n-4} and C_nH_{2n-8}. This change in series is accompanied with a corresponding increase in specific gravity. These viscous hydrocarbons evidently approach the constituents of the asphaltic oils and natural tars. It is easy to see how petroleum is converted by slow evaporation in nature into the great beds of tars and asphalts, and it affords the most probable explanation of their formation.

The hydrocarbons described in this paper, with their boiling points and specific gravity, are brought together in the following table:

HYDROCARBONS SEPARATED FROM SANTA BARBARA (CAL.) PETROLEUM.

	Symbol.	Boiling Point.	Specific Gravity at 20°.
Hydrocarbon	$C_{13}H_{24}$	150°–155°, 60 mm.	0.8621
"	$C_{16}H_{30}$	175°–180°, "	0.8808
"	$C_{17}H_{30}$	190°–195°, "	0.8919
"	$C_{18}H_{32}$	210°–215°, "	0.8996
"	$C_{24}H_{44}$	250°–255°, "	0.9299
"	$C_{27}H_{46}$	310°–315°, "	0.9451
"	$C_{29}H_{50}$	340°–345°, "	0.9778

IV. SEPARATION OF SOLID PARAFFINE HYDROCARBONS FROM PETROLEUM WITHOUT EVAPORATION.

BY CHARLES F. MABERY AND OTTO J. SIEPLEIN.

By the method of distillation, which is the only means for the separation of the petroleum hydrocarbons, it is not possible to determine whether the solid paraffine hydrocarbons are contained in the crude oil or whether they may not be formed by decomposition.

As a direct proof that the solid hydrocarbons are actually contained in petroleum we have separated them without distillation. Three kilos of an average specimen of Pennsylvania crude petroleum was allowed to stand in a shallow pan exposed to a current of air in a strong flue draft

for thirty days. The change was shown by the increase in specific gravity:

Specific gravity at 15° before exposure. Dec. 9.	Dec. 12.	Jan. 8.
0.000	0.840	0.862

When taken from the flue, January 8, the residue weighed one kilo, which showed a loss of 66.67 per cent. The original oil distilled as follows:

50°-150°.	150°-200°.	200°-250°.	250°-300°.	+300°.
21 per cent.	11 per cent.	11 per cent.	13 per cent.	42 per cent.

The residue above 300° is, therefore, about the same in weight as the residue left by evaporation. That the loss by evaporation had practically ceased at the end of one month was shown by allowing the residue to stand one year in the same place, exposed to draft as before. But there was no change in weight nor in specific gravity.

A combustion of the crude oil gave the following percentages of carbon and hydrogen:

0.1968 gram of the oil gave 0.4915 gram CO_2 and 0.2512 gram H_2O.

C	85.51
H	14.18

Combustion of the residue after 30 days' evaporation:

0.1559 gram of the oil gave 0.4925 gram CO_2 and 0.1559 gram H_2O.

C	86.16
H	13.69

Evaporation of the portions with lower boiling points, which form the greater part of the series C_nH_{2n+2}, leaves a larger proportion of series poorer in hydrogen, C_nH_{2n} and C_nH_{2n-2} corresponding to the composition shown by analyses.

On cooling with ice the residue from evaporation became quite solid.

On distillation, 28 per cent came over below 30°, 6 per cent at 300°–360°, with a residue above 360° of 66 per cent.

The amount of solid hydrocarbons in the residue was determined by the method suggested by Zaliozieck. 50 grams of the residue with fusel oil, mostly isoamyl alcohol, was allowed to stand at 0° for 24 hours; 250 grams alcohol was then added and the precipitate collected on a

filter, and washed with a mixture of fusel oil and alcohol. The precipitate on the filter was then placed in an extraction apparatus, and the solid extracted with benzol. After evaporation of the benzol, the residue was heated to 140° for one hour to remove the last traces of fusel oil. 19.8 grams of a greenish black solid remained, melting at 32°, equivalent to 39.6 per cent of the heavy residue or to 14 per cent of the original oil before evaporation.

The solid was again dissolved in fusel oil and precipitated by alcohol, giving a smaller quantity of solid melting at 45°. This treatment repeated gave a light brown solid melting at 57°. The latter was then dissolved in ether and precipitated by alcohol, which gave a lighter colored solid; another repetition gave a white solid melting at 61°. Its specific gravity was 0.7966 at 70°, corresponding to that of paraffine, and a combustion gave percentages of carbon and hydrogen required for paraffine hydrocarbons.

0.1511 gram of the solid gave 0.4730 gram CO_2 and 0.1984 gram H_2O.

C	85.37
H	14.69

The specific gravity, melting point, and composition of this substance indicate that it was composed of paraffine hydrocarbons, and demonstrate the presence of the solid paraffine hydrocarbons in Pennsylvania petroleum.

Paraffine collected from heavy distillates in the refinery is therefore obtained as it exists from the original crude oil, and it is not formed during distillation. Indeed, as explained in another paper, it cannot be formed; for any decomposition of petroleum hydrocarbons by heat removes hydrogen with a conversion of the hydrocarbon into a lower series; for example, of the paraffine hydrocarbons of the series C_nH_{2n+2} into the series C_nH_{2n}, C_nH_{2n-2}, etc., and perhaps also forming the methylenes and condensed methylenes. Such changes do not involve an absorption of oxygen into the hydrocarbon molecule, but a removal of hydrogen by oxygen as water. That oxygen compounds of the nature of phenols are found in petroleum from various fields has been fully demonstrated independently by Richardson and by Mabery (data not published), and it is quite probable that most petroleum contain these bodies to a greater or less extent; but they have been formed by natural processes.

In ordinary refinery distillation, there is probably little decomposition below 300° C., but at this point cracking begins and increases rapidly to the end. There are doubtless reactions at higher temperatures between

nitrogen, sulphur, and oxygen compounds. Then the breaking down in series begins with loss of hydrogen, through the asphaltic hydrocarbons, until finally coke is reached, which forms a considerable proportion of the products of refining.

V. THE SOLID PARAFFINE HYDROCARBONS THAT COLLECT IN CERTAIN OIL WELLS IN PENNSYLVANIA.

In attempting to determine the series of hydrocarbons, and members of the series that form the solid constituents of Pennsylvania petroleum, it seemed of interest to examine the semi-solid product that collects in considerable quantites in some of the Pennsylvania wells, especially at Coreopolis, Pa. The Petrolatum Company collects large quantities of this pasty substance from their wells and from it manufacture various preparations such as vaseline and cosmoline. The crude product is obtained in the form of a light-yellow pasty mass, from which it is impossible to separate a solid by pressure in filter paper or by filtration. It evidently consists of an emulsion of the high boiling oils with the solid hydrocarbons which no doubt are in part dissolved in the oily constituents.

Having obtained several gallons of this substance through the kindness of the Coreopolis Petrolatum Company in October, 1898, I undertook an examination of it with the principal object of proving the presence of solid hydrocarbons, and identifying their composition as to the series and molecular formulas, for comparison with the solid hydrocarbons which I have separated from Pennsylvania crude oil and from commercial paraffine. These semi-solid emulsions have no doubt been formed by evaporation of the lighter constituents of petroleum, and the solid hydrocarbons are therefore what were contained in the original petroleum. It also afforded an opportunity to confirm the presence of the solid constituents of paraffine in crude petroleum, a question concerning which a doubt is often expressed by refiners.

The specimen received was in the form of a thick paste, with a specific gravity at 60° of 0.8345. In beginning the distillation, 9380 grams were distilled in a porcelain still under a tension of 50 mm. and the distillates collected in the following quantities:

	-195°	195°-200°	200°-245°	245°-265°	265°-285°
Grams	905	865	895	850	830
	285°-315°	315°-330°	330°-342°		Residue.
Grams	200	790	885		3000

Distillation of these fractions was continued within 10°, 5°, and 2°, until after the sixth distillation larger quantities collected at the following temperatures:

242°–244° 268°–270° 280°–282° 308°–310° 328°–330°

340°–342° 352°–354 ° 368°–370° 382°–384°

Since the distillates below 268° showed by their thin pasty condition that they contained only small proportion of solid hydrocarbon, no attempts were made to separate their constituents. The fraction 272°–274° gave as its specific gravity at 20° 0.8116. A combustion gave the following percentages of carbon and hydrogen:

0.1600 gram of the substance gave 0.5058 gram CO_2 and 0.1963 gram H_2O.

Calculated for $C_{25}H_{48}$.	Found
86.21	86.22
13.79	13.73

This fraction, therefore, consisted mainly of a hydrocarbon of the series C_nH_{2n-2}, and the same will appear in the higher fractions to be described.

On cooling the distillates with salt and ice, and attempting to separate the solid by filtration under pressure, scarcely any of the solid remained on the filter, so complete was the emulsion. But on trying the solubility in ether and alcohol, such a wide difference was observed between the crystalline and amorphous solid, it afforded an easy means of separation.

The distillate 272°–274°, 30 mm., was therefore dissolved in a suitable mixture of ether and alcohol cooled with salt and ice and filtered cold. The solid collected was pressed and the crystallization repeated, which gave a perfectly white crystalline hydrocarbon, melting point 50°–51°. It gave as its specific gravity at 60°, 0.7900. Determinations of carbon and hydrogen gave percentages required for the series C_nH_{2n+2}.

0.1516 gram of the substance gave 0.4728 gram CO_2 and 0.1973 gram H_2O.

	Calculated for Tetracosane, $C_{24}H_{50}$.	Found.
C	85.21	85.06
H	14.79	14.56

The quantity of the solid hydrocarbon obtained was small, evidently not sufficient to influence the proportions of carbon and hydrogen in the unfiltered distillate. While the amount obtained was not enough for a determination of its molecular weight, its melting point and specific gravity, the same as those of the hydrocarbon tetracosane separated from paraffine distillate 272°–274°, indicate that it has the same composition.

Tetracosane obtained by Krafft,* by reduction of the ketone derived from barium stearate and barium heptylate, melted at 51°. But the specific gravity of Krafft's hydrocarbon was somewhat lower than that of the hydrocarbon from petroleum.

The quantities of the distillates between 274° and 316° were too small to permit of a separation of crystalline hydrocarbons in sufficient amounts for identification of individual constituents.

The pasty solid collected at 316°–318°, 50 mm., yielded a solid hydrocarbon by crystallization from alcohol and ether that melted at 66°. The crude distillate gave as its specific gravity at 20°, 0.8212. A combustion gave values required for the series C_nH_{2n-2}.

0.1564 gram of the substance gave 0.4935 gram CO_2 and 0.1930 gram H_2O.

	Calculated for Hentricontane, $C_{28}H_{54}$.	Found.
C	86.15	86.05
H	13.85	13.80

The purified solid gave as its specific gravity at 70°, 0.7997.

A combustion gave numbers for carbon and hydrogen required for the series C_nH_{2n+2}.

0.1499 gram of the substance gave 0.4698 gram CO_2 and 0.1969 gram H_2O.

	Calculated for $C_{31}H_{64}$.	Found.
C	85.31	85.45
H	14.69	14.69

The formula of this hydrocarbon was further verified by its molecular weight.

0.3648 gram of this substance and 12.12 grams naphthaline gave a depression of 0.471.

Calculated for $C_{31}H_{64}$.	Found.
436	441

* Ber. Deutsch. chem. Gesellsch., **15**, 1718 (1882).

From the ketone palmiton, $C_{31}H_{62}O$, Krafft * prepared Hentricontane, $C_{31}H_{64}$, M. P. 68°.1, which differs but slightly from that of the hydrocarbon separated from petroleum, 66°.

Since the solid hydrocarbon formed such a small proportion of the original distillate that it did not affect materially the composition of the latter, this solid evidently could not be compared with the hydrocarbon separated from the corresponding distillate from paraffine nor that from crude Pennsylvania petroleum, for the predominating constituents should materially affect the boiling points of all the minor solid constituents. This is shown to be true by the high molecular weights and high melting points of the hydrocarbons separated from Coreopolis distillates so far as they could be determined. The distillate collected at 328°–330°, 50 mm., after filtration from the solid, gave as its specific gravity at 70°, 0.8235. After crystallization from ether and alcohol, the white crystalline solid gave as its specific gravity at 70°, 0.7982. The proportions of carbon and hydrogen given by combustion supported the formula of the series C_nH_{2n+2}. The original distillate gave as its specific gravity 0.8217. A combustion gave the following percentages of carbon and hydrogen.

0.1586 gram of the substance gave 0.4995 gram CO_2 and 0.1925 gram H_2O.

	Calculated for $C_{29}H_{56}$.	Found.
C	86.14	85.86
H	13.86	13.57

The solid purified from ether and alcohol gave proportions of carbon and hydrogen corresponding to the series C_nH_{2n+2}.

0.1549 gram of the solid gave 0.4842 gram CO_2 and 0.2075 gram H_2O.

	Calculated for $C_{32}H_{66}$.	Found.
C	85.33	85.25
H	14.67	14.98

The melting point of the crystalline hydrocarbon was found to be 67°–68°. Its molecular weight at the boiling point of benzol and also at the freezing point of naphthaline indicated the next higher homologue, $C_{32}H_{66}$, dotricontane, but the small quantity of substance available for this determination was not sufficient to yield satisfactory results.

The specific gravity of the unpurified distillate 342°–344°, 50 mm., was 0.8288; after separation of the solid by freezing and purification

* Ber. Deutsch. chem. Gesellsch., **15**, 1714.

from ether and alcohol its specific gravity was 0.8005 at 75°. Melting point of the purified hydrocarbon, 68°–70°. The unpurified distillate gave percentages of carbon and hydrogen corresponding to the series C_nH_{2n-2}.

0.1517 gram of the substance gave 0.4784 gram CO_2 and 0.1850 gram H_2O.

	Calculated for $C_{30}H_{58}$.	Found.
C	86.12	86.06
H	13.88	13.64

The purified solid gave proportions of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1544 gram of the solid gave 0.4816 gram CO_2 and 0.2060 gram H_2O.

	Calculated for $C_{32}H_{66}$.	Found.
C	85.33	85.06
H	14.67	14.92

The molecular weight as determined by the boiling point method confirmed the formula $C_{32}H_{66}$.

0.5127 gram of the substance and 12.23 grams benzol gave a depression of 0°.654.

Calculated for $C_{32}H_{66}$.	Found.
438	442

As mentioned above, the solid hydrocarbons form a small proportion of the original oil, and the small amounts that collect at 328°–330° and 340°–342° have doubtless nearly the same composition, $C_{32}H_{66}$.

The distillate 366°–368°, 50 mm., before treatment, had the specific gravity 0.8312, and the solid hydrocarbon separated by freezing, filtration, and crystallization from ether and alcohol, the specific gravity at 80°, 0.8009. The purified solid melted at 71°–72°. The proportions of carbon and hydrogen in the unpurified distillate corresponded to the formula C_nH_{2n-2}.

0.1485 gram of the substance gave 0.4982 gram CO_2 and 0.1851 gram H_2O.

	Calculated for $C_{31}H_{60}$.	Found.
C	86.11	85.96
H	13.89	13.94

The solid separated from the fraction 366°–368°, after purification, gave on analysis 85.41 per cent carbon and 14.74 per cent hydrogen, corresponding to the series C_nH_{2n+2}, was present in only small quantity, and probably differed but slightly from the hydrocarbon contained in the fraction 342°–344°.

The close agreement in composition of the untreated distillate, before removing the solid hydrocarbon, to the series C_nH_{2n-2}, is due, as explained above, to the very small proportion of the solid hydrocarbon, C_nH_{2n+2}. The oils separated by filtration are evidently composed for the greater part of the series C_nH_{2n-2}, although the low percentage of hydrogen may indicate the presence in small amounts of a series even poorer in hydrogen.

The untreated distillate 380°–384°, 50 mm., gave as its specific gravity 0.8336, and the solid hydrocarbon obtained by freezing, filtration, and crystallization from ether and alcohol, 0.8052 at 80°. Melting point, 76°. Determinations of carbon and hydrogen indicated the series C_nH_{2n-2}.

0.1560 gram of the substance gave 0.4898 gram CO_2 and 0.1943 gram H_2O.

	Calculated for $C_{34}H_{66}$.	Found.
C	86.08	95.82
H	13.92	13.93

A combustion of the purified solid gave percentages of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1501 gram of the solid gave 0.4695 gram CO_2 and 0.1974 gram H_2O.

	Calculated for $B_{35}H_{72}$.	Found.
C	85.37	85.33
H	14.63	14.71

The molecular weight of the solid as determined by the boiling point method corresponded to the same formula.

1.0012 gram of the substance and 24.72 grams benzol gave a rise of 0°.212.

Calculated for $C_{35}H_{72}$.	Found.
492	490

As the molecular weights of the hydrocarbons of these series increase the determinations become more and more difficult and uncertain. The values obtained support, together with other data, the formulas given. With the high boiling liquids there is less trouble than with solids.

As formerly explained, the freezing point of benzol cannot be relied on for solids with molecular weights much above $C_{20}H_{42}$. At its boiling point benzol can be depended on for a somewhat higher range, but becomes uncertain with hydrocarbons in the vicinity of $C_{30}H_{62}$. Other solvents are equally uncertain, on account of a lack of solubility or uncertain influence of the dissolved substance on the freezing point. After long trial with naphthaline, which promised reliable results on account of its free solvent power and large depression, we found that the substances that had melting points not far removed from that of naphthaline gave variations in depression too great for reliable calculations of molecular weights.

SOLID HYDROCARBONS IN PENNSYLVANIA OIL WELLS.

	Symbol.	Melting point.	Specific gravity.
Tetracosane	$C_{24}H_{50}$	50°–51°	0.7900 at 60°
Hentricontane	$C_{31}H_{64}$	66°	0.7997 at 70°
Dotricontane	$C_{32}H_{66}$	67°–68°	8.8005 at 75°
Tetratricontane	$C_{34}H_{66}$	71°–72°	0.8009 at 80°
Pentatricontane	$C_{35}H_{72}$	76°	0.8052 at 80°

Hydrocarbons of the series C_nH_{2n+2} have now been identified in Pennsylvania petroleum in continuous series, with but few members wanting from butane, C_4H_{10}, B. P. —10°, to pentatricontane, $C_{35}H_{72}$, B. P. 380°–384°, 50 mm.

VI. COMPOSITION OF COMMERCIAL PARAFFINE.*

It has been questionable, even with refiners of petroleum of long experience, as to whether paraffine is actually present in the crude oil or whether it is a result of change during the process of refining. It therefore seemed of interest to ascertain whether the hydrocarbons of which commercial paraffine is composed are identical with the solid constituents of the crude oils that yield paraffine.

The method of distillation was the same as that employed in distilling the crude oil, except that it was found necessary to pack the neck of the flask with a thick coating of asbestos. With exclusion of air it was found that paraffine could be distilled indefinitely with no decomposition. But introduction of air, either by leaks or by accident, caused serious decomposition, as shown by the dark color and disagreeable odor of the distillates.

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* A part of the work described in this paper was performed by Mr. H. R. Payne, and formed the subject of a thesis for the degree of Bachelor of Science.

1500 grams of the best commercial paraffine was distilled *in vacuo* under 40 mm., and the distillates were collected at first within 10°, then 5°, and finally within 2°, altogether seven times. The lowest distillate collected below 250°, and the final residue above 350° was only 30 grams. All the distillates were colorless, except the residue, which was slightly brown, and nearly odorless. The distillates collected in larger quantities at temperatures corresponding to those of hydrocarbons separated from the crude oil as follows:

256°–258°	90 grams	316°–318°	35 grams
272°–274°	45 "	332°–334°	20 "
282°–284°	70 "	346°–348°	40 "
292°–294°	30 "		

TRICOSANE, $C_{23}H_{48}$, B. P. 256°–258° (40 mm.).

The distillate 256°–258° melted without purification at 48°, and the melting point was not raised by crystallization from alcohol and ether. Tricosane obtained by Krafft * melted at 47°.7. Its specific gravity was ascertained above its melting point.

60°	0.7836	70°	0.7814	80°	0.7807

The specific gravity of tricosane from petroleum differs materially from the specific gravity of this hydrocarbon which Krafft obtained from the ketone, lauron.

47°.7	0.7785	80°.8	0.7570	88°.8	0.7456

A combustion of this hydrocarbon gave percentages of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1510 gram of the substance gave 0.4710 gram CO_2 and 0.1989 gram H_2O.

	Calculated for $C_{23}H_{48}$.	Found.
C	85.20	85.06
H	14.80	14.73

A determination of its molecular weight at the boiling point of benzol gave a value required for tricosane.

* Ber. d. chem. Gesellsch., **15**, 1713 (1882).

0.8907 gram of the solid and 24.24 grams benzol gave a rise of 0°.295.

Calculated for $C_{23}H_{48}$.	Found.
324	319

TETRACOSANE, $C_{24}H_{50}$, B. P. 272°–274° (40 mm.).

This distillate melted without purification at 50°–51°, which was not changed by crystallization from alcohol and ether. Krafft's tetracosane obtained from the ketone derived from barium stearate and barium heptylate melted at 51°.1. The quantity obtained of tetracosane was not sufficient to determine its specific gravity.

This hydrocarbon was shown to belong to the series C_nH_{2n+2} by the following combustions:

I. 0.1424 gram of the substance gave 0.4451 gram CO_2 and 0.1923 gram H_2O.
II. 0.1460 gram of the substance gave 0.4551 gram CO_2 and 0.1955 gram H_2O.
III. 0.1443 gram of the substance gave 0.4502 gram CO_2 and 0.1924 gram H_2O.

	Calculated for $C_{24}H_{50}$.	Found. I.	II.	III.
C	85.21	85.25	85.00	85.08
H	14.79	14.96	14.97	14.91

The formula was verified by a determination of its molecular weight.

3.0316 grams of the oil and 22.42 grams benzol gave a rise of 1°.034.

Calculated for $C_{24}H_{50}$.	Found.
338	335.

PENTACOSANE, $C_{25}H_{52}$, B. P. 282°–284° (40 mm.).

The melting point of the unpurified distillate 282°–284° was 53°–54°. After crystallization from ether and alcohol, it melted at 54°.

Its specific gravity was determined above its melting point:

60°	0.7911	80°	0.7870
70°	0.7881	90°	0.7854

A combustion gave percentages of carbon and hydrogen required for the formula C_nH_{2n+2}.

0.1467 gram of the substance gave 0.4578 gram CO_2 and 0.1950 gram H_2O.

	Calculated for $C_{25}H_{52}$.	Found.
C	85.23	85.09
H	14.77	14.88

The formula was identified by a determination of its molecular weight.

1.4324 grams of the substance and 8.5282 grams benzol gave a rise of 1°.265.

Calculated for $C_{25}H_{52}$.	Found.
352	354

Hexacosane, $C_{26}H_{54}$, B. P. 294°–296° (40 mm.)

After the seventh distillation, 25 grams collected at 294°–296°, that gave as its melting point 55°–56°, and this was not changed by crystallization from ether and alcohol. It gave as its specific gravity above its melting point:

60°	0.7938	80°	0.7893
70°	0.7918	90°	0.7879

The percentages of carbon and hydrogen obtained by combustion corresponded to the series C_nH_{2n+2}.

0.1526 gram of the solid gave 0.4757 gram CO_2 and 0.2027 gram H_2O.

	Calculated for $C_{26}H_{54}$.	Found.
C	85.23	85.02
H	14.77	14.86

The molecular weight found at the boiling point of benzol verified the formula.

1.6742 grams of the substance and 13.151 grams benzol gave a rise of 0°.93.

Calculated for $C_{26}H_{54}$.	Found.
366	365

Octocosane, $C_{28}H_{58}$, B. P. 316°–318° (40 mm.).

At 316°–318°, 35 grams collected after the seventh distillation that melted at 60°, which was not changed by crystallization from ether and alcohol. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1586 gram of the oil gave 0.4954 gram CO_2 and 0.2122 gram H_2O.

	Calculated for $C_{28}H_{58}$.	Found.
C	85.28	85.17
H	14.72	14.96

A determination of its molecular weight corresponded to the formula $C_{28}H_{58}$.

I. 1.3337 gram of the solid and 23.73 grams benzol gave a rise of 0°.362.

II. 1.7964 gram of the solid and 21.96 grams benzol gave a rise of 0°.53.

Calculated for $C_{28}H_{58}$.	Found. I.	Found. II.
394	397	396

NONOCOSANE, $C_{29}H_{60}$, B. P. 346°-348° (40 mm.).

At 346°-348° 40 grams collected; melting point, 62°-63°. It gave on combustion percentages of carbon and hydrogen for the series C_nH_{2n+2}.

0.1520 gram of the solid gave 0.4752 gram CO_2 and 0.2062 gram H_2O.

	Calculated for $C_{29}H_{60}$.	Found.
C	85.28	85.27
H	14.72	14.87

Its molecular weight was found to be as follows:

I. 1.6181 gram of the substance and 23.57 grams benzol gave a rise of 0°.41.

II. 1.6236 gram of the substance and 23.99 grams benzol gave a rise of 0°.402.

Calculated for $C_{29}H_{60}$.	Found. I.	Found. II.
406	405	408

That the solid distilling above 350° has the composition of the series C_nH_{2n+2} is shown by the following combustion:

0.1469 gram of the solid gave 0.4581 gram CO_2 and 0.1947 gram H_2O.

	Calculated for $C_{30}H_{62}$.	Found.
C	84.31	85.04
H	14.69	14.82

Since only two per cent of the original paraffine taken for distillation remained as a residue at 350°, the solid hydrocarbons which compose the main body of paraffine produced in the refinery are evidently members of the series C_nH_{2n+2}. They do not contain oxygen, as frequently stated, — at least the hydrocarbons that can be distilled. It is not reasonable to assume that they have been formed by cracking from other constituents, since such decompositions give rise to hydrocarbons of lower molecular weights. It is well known that paraffine may be decomposed completely by heat when exposed to air into lower hydrocarbons. In mass we have found that it may be distilled indefinitely by exclusion of air, but it cannot be distilled in air without decomposition.

Thorpe and Young * subjected shale paraffine to distillation under pressure in a bent tube so arranged that the paraffine could be repeatedly distilled. The distillation was continued until the solid was converted into bodies that remained liquid at ordinary temperatures. This liquid proved to consist of two series of hydrocarbons; of the series C_nH_{2n+2}, the hydrocarbons C_5H_{12} to $C_{11}H_{24}$ were identified, and of the series C_nH_{2n} the ethylene hydrocarbons, C_5H_{10} to $C_{11}H_{22}$.

It is our intention to examine the products of the distillation of paraffine in air to observe the changes in cracking. It is an interesting question as to whether any relation exists between the paraffine hydrocarbons and the methylenes with reference to the formation of these bodies in their organic origin, and whether the series are interconvertible by natural agencies.

Hydrocarbons in Commercial Paraffine.

	Symbol.	Melting Points.	Specific Gravity.
Tricosane	$C_{23}H_{48}$	48°	0.7886 at 60°
Tetracosane	$C_{24}H_{50}$	50°–51°	
Pentacosane	$C_{25}H_{52}$	53°–54°	0.7941 at 60°
Hexacosane	$C_{26}H_{54}$	55°–56°	0.7968 at 60°
Octocosane	$C_{28}H_{58}$	60°	
Nonocosane	$C_{29}H_{60}$	62°–63°	

* Ber. d. deutsch. Gesellsch., 5, 556 (1872).

VII. COMPOSITION OF COMMERCIAL VASELINE, COSMOLINE, AND SIMILAR PRODUCTS.

After ascertaining the composition of the constituents of Pennsylvania petroleum with high boiling points, and the composition of the semi-solid product used at Coreopolis for the manufacture of the medicinal preparations, it seemed of interest to investigate the composition of the commercial products for comparison with specimens obtained directly from the wells. On account of the very high boiling points, it is only possible to apply distillation *in vacuo*. Under 15 mm., 100 grams of vaseline (Ceroleum) distilled in the following proportions.

	-250°	250°-275°	275°-300°	300°-325°	325-350°	350°-360°	Residue.
Grams	14	22	14	18	7	20	6

The distillates were light yellow in color, and when melted showed a slight fluorescence. Below 250° the distillate was a heavy viscous liquid, the others all semi-solid, and the residue was colored brown. To ascertain whether solids could be separated from these distillates, the fraction 250°–275° was dissolved in ether and sufficient alcohol added to precipitate the solid hydrocarbon. The solid was again dissolved in ether and precipitated by alcohol. After filtration it showed no greasy feel and melted at 70°. After similar treatment, from the fraction 350°–360°, a solid was obtained which melted at 77°–78°. These solids resembled in all respects the solid paraffine hydrocarbons. It is therefore evident that vaseline is composed of heavy oils such as have been identified as forming the portions of Pennsylvania petroleum with high boiling points, and Coreopolis heavy oil, hydrocarbons of the series C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-4}, together with solid paraffine hydrocarbons. The quantity of solid compounds present is sufficient to saturate the oil and in slight excess to form an emulsion of the desired consistency.

What is known as "scale" paraffine in the refineries is composed of the solid hydrocarbons, with enough of the heavy oils to form a greasy solid. But the solid constituents are hydrocarbons of the same series, C_nH_{2n+2}, which cannot be changed into other forms without decomposition. These hydrocarbons are only sparingly soluble in the liquid hydrocarbons of lower boiling points of the same series; but they dissolve more freely in the series with high boiling points, C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-4}.

Since the work described in these papers was begun, ten years ago, I have received efficient aid from the following assistants in distillation:

Messrs. C. Lindmueller, D. H. Walker, C. R. Cummins, and H. A. Triebing; in distillation and analysis, Mr. C. S. Richards; analysis and molecular weight determinations, valuable aid from Mr. O. J. Sieplein.

It is my intention to make later a summarization in a separate paper of the results published from the beginning in this series of papers on petroleum.